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AUTHOR(S):

Kurakado, Masahiko; Takabatake, Toshiro; Mazaki, Hiromasa

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Superconducting Transition Temperature of Technetium and Lead

Masahiko KURAKADO, Toshiro TAKABATAKE, and Hiromasa MAZAKI*

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Superconducting transition temperatures of technetium and lead were determined by means of resistive transition. Technetium samples were prepared by electrodeposition and reduction. Lead samples were prepared by the usual vacuum evaporation. The transition temperatures are 7.46± 0.05 K for technetium and $7.25_7 \pm 0.01$ K for lead.

I. INTRODUCTION

Since there is no stable isotope of technetium, the study of the superconducting properties was at earlier stage limited to measurements of the transition temperature, *Tc*. With gram quantities of metallic technetium reprocessed from nuclear fuel, Sekula, Kernohan, and Love[1] investigated the detailed superconducting properties.

A method to prepare metallic technetium by means of electrodeposition and reduction was reported by Byers and Stump.[2] We modified the method paying great care to radioactive contaminations and established a conventional device to prepare metallic technetium which can be used for investigations of the superconducting properties. With the sample prepared, *Tc* of technetium was measured by means of electroresistivity. Further experiment on the magnetic properties of technetium in the superconducting state is in progress.

For confirmation of the whole experimental procedure involving temperature control and calibrations of a germanium thermometer, *Tc* of lead was also measured. Details of our investigation are reported here.

II. EXPERIMENTAL

1. Sample Preparation

Preparation of metallic technetium was made by electrodeposition and reduction. The working solution of electrodeposition consists of 20-ml H_2SO_4 solution (pH 1.0), 50-mg NH_4F, and some of the aqueous solution of $NH_4{}^{99}TcO_4$ (20 μ Ci). The cathode is a thin film of nichrome spattered on a ceramic base (5.5 × 8.5 × 0.6 mm) and the anode is a platinum wire of 0.3 mm in diameter and 8 cm long in zigzag patern.

The electrodeposition was continued for 22～23 h with a current of 0.7～1 mA/mm^2. In order to achieve electrodeposition of technetium, the electrolyte was stirred by bubbling pure nitrogen gas through a capillary tube. After the deposition, 90～96% of technetium in the bath was recovered on the cathode. In Fig. 1 is shown the construction of the device of electrodeposition.

* 倉門雅彦，高畠敏郎，間崎啓匡：Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Kyoto.

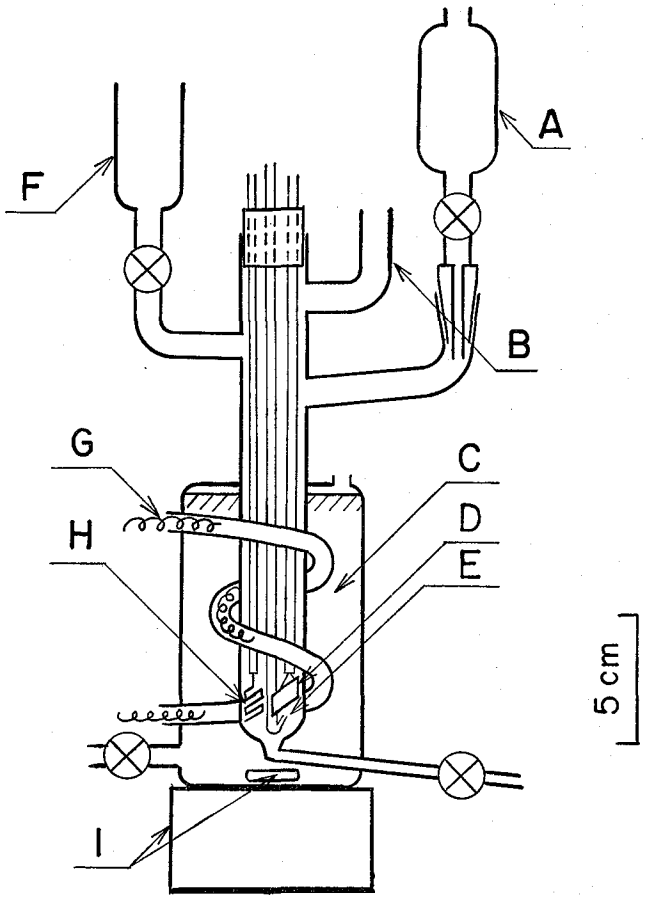

Fig. 1. The device for electrodeposition of technetium; A) working solution inlet, B) gas outlet, C) bath of silicon oil, D) cathode on which technetium is deposited, E) capillary tube for bubbling pure nitrogen gas, F) water inlet, G) heater, H) anode, I) magnetic stirrer.

For reduction of technetium deposited on the cathode, a reduction system was constructed, of which schematic diagram is shown in Fig. 2. The reduction chamber is quartz tube of 20 mm in diameter and 100 cm long, filled with oxygen free pure hydrogen supplied through a 30-cm long Pd leak, and one section of the chamber is heated in an electric furnace. The technetium sample is put on a quartz boat together with some pieces of titanium, by which outer gases from the sample and the surroundings during heat treatment are absorbed.

Before heat treatment of the sample, the reduction chamber was lavaged at least three times at 1000°C by pure hydrogen gas. Then the sample was transferred into the heat section of the quartz tube and was reduced for several hours. After the reduction, the sample shows the silvery metallic color of somewhat dull luster characteristic of technetium. The thickness was estimated to be about 5×10^4 Å which is considered to be bulk material in superconducting behavior. The electric

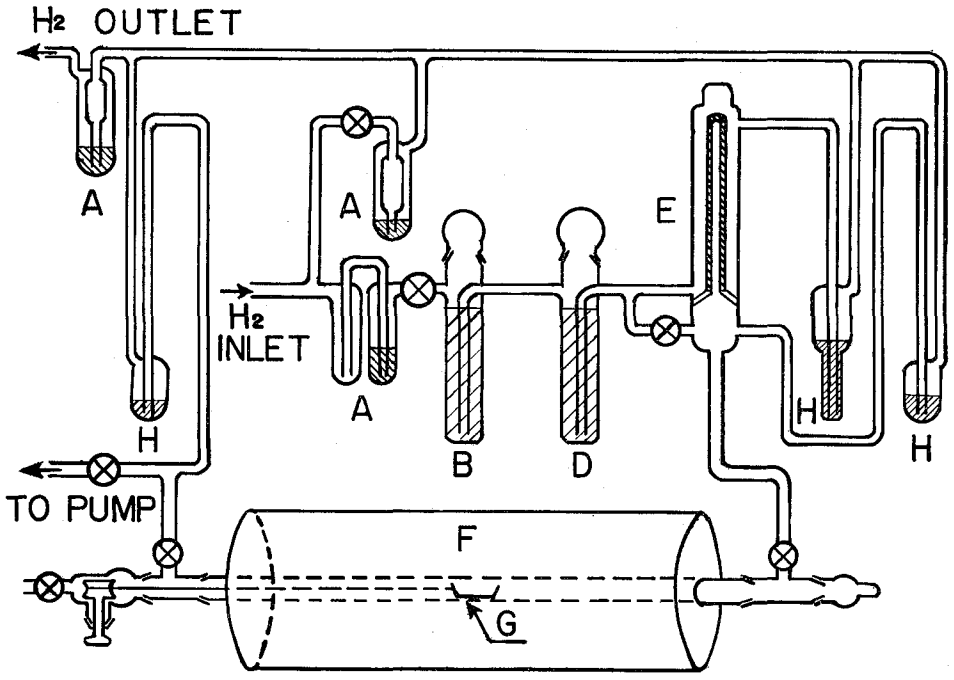

Fig. 2. The device for reduction of technetium; A) oil flow meter, B) $CaCl_2$ to remove H_2O, D) P_2O_5 to remove H_2O, E) Pd leak, F) electric furnace, G) quartz boat, H) mercury.

resistance is 1～2 ohm. The value of Γ, the ratio of resistance at room temperature to the resistance just above Tc, could not be determined because technetium was deposited on the nichrome film.

In order to make sure the production of metallic technetium, X-ray analysis of the sample was performed. We found that the sample has the hcp structure with lattice constants $a=2.741$ Å and $c=4.398$ Å. Impurity analysis was carefully made by X-ray fluorescence spectroscopy. Trace elements of Ni, Cu, and Fe were identified. However, by the preliminary electrodeposition of technetium on the cathode, these impurities contained in the technetium sample were minimized.

Preparation of the lead sample (99.999 %) was made by the usual vacuum evaporation on a microscope cover glass ($18\times9\times0.2$ mm). The film of lead has a belt shape of 1×10 mm and the thickness is about 10^4 Å. The value of Γ is 88 for the sample evapolated at the pressure of 3.2×10^{-6} mmHg and 50 at 1×10^{-5} mmHg.

2. Calibration of a Germanium Thermometer

The measurements from 1.744 to 20.332 K were made using a capsule-type germanium thermometer manufactured by Scientific Instruments Inc. The resistance of the thermometer was measured by a four-terminal method where a digital voltmeter with 0.1-μV resolution was used. The constant current through the thermometer was 10 μA with stability of 5×10^{-3} %. The germanium thermometer was calibrated against the vapor-pressure thermometer in the range of 1.744～4.212 K

(helium) and of 14.194~20.332 K (hydrogen). According to Martin,[3] the best representation of the variation of resistance of the thermometer as a function of temperature can be given by a polynomial of the form

$$\ln R = \sum_{n=1}^{m} A_n (\ln T)^{n-1} .$$

For the present thermometer, the standard deviation of the calibration points does not change significantly for $m=5\sim10$. Thus we adpoted the mean value of the calibration points for $m=5\sim10$. Since in the range of 4.212~14.194 K, no experimental calibration was made, the calibration points in this range were calculated by means of least-squares fitting of the above equation. The calibration curve thus determined was found to be accurate within 10 mK and the relative change in temperature can be measured with the accuracy of 0.1 mK.

3. Measurements of *Tc*

In Fig. 3 is shown the block diagram for measurements of the resistance of technetium or lead sample. The resistance was measured across the samples prepared for the conventional ac four-terminal method (10 μA, 1 kHz, supplied from a lock-in amplifier). In order to observe the quite small voltage (~10 μV) across the samples, a recorder was used through a lock-in amplifier. To monitor the current through the samples, the voltage across a standard resistance (100 ohm) was also measured. A 10^4-ohm resistance was used in series to keep the current through the sample constant.

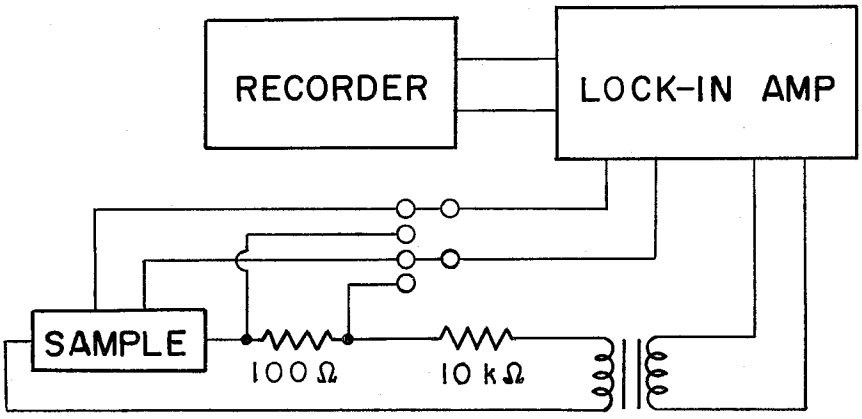

Fig. 3. Block diagram for measurements of the resistance of technetium or lead sample.

The sample holder in a cryostat is shown in Fig. 4. In order to avoid any difference in temperature between the sample and the germanium thermometer, both of them are set in a copper block. For better thermal contact, Apiezon "N" grease is used. Electrical connections are made through 0.2-mm ϕ enamel-coating copper wires. To acheive good thermal shieldings, the wires are wound and fixed with varnish, GE 7031, around the suspension pole at the top of the sample room

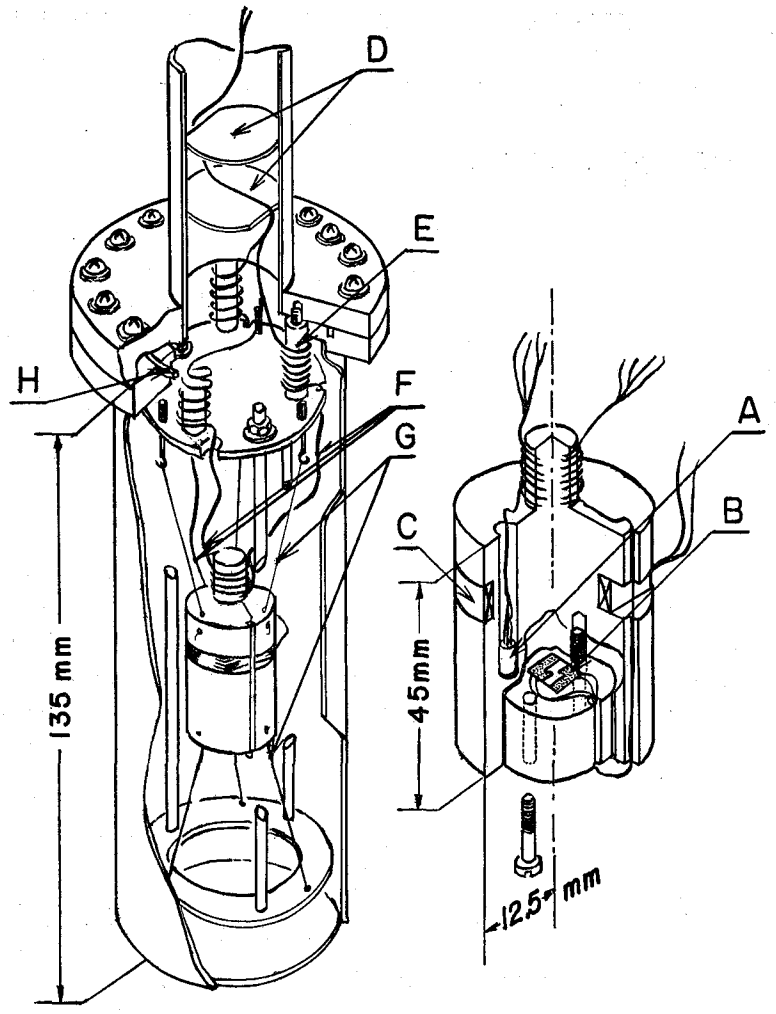

Fig. 4. The construction of the sample holder; A) germanium thermometer, B) sample, C) heater, D) heat radiation shield, E) heat station, F) superconducting wires, G) silk threads, H) indium seal.

and also around the copper block before reaching the sample and the thermometer. Furthermore, superconducting wires (Nb-Ti) are partly used because of the poor thermal conductivity. The copper block is suspended by silk thread in the sample room.

The temperature control was made with duplicated Karma wires (100 ohm/m) wound and fixed around the copper block. Since the electric current for heating flows forward and backward through the duplicated wires, no magnetic effect on the sample should appear.

III. RESULTS AND DISCUSSION

It was found that the observed transition temperature of lead depends on the

electric power for heating. For poor vacuum in the sample room, there is certainly heat leak from the copper block and consequently more electric power is needed to raise the temperature of the copper block above 4.2 K. This results in the unhomogeneous temperature distribution in the sample holder. Therefore, the vacuum in the sample room should be good enough to minimize the temperature difference between the sample and the germanium thermometer. In Fig. 5, the

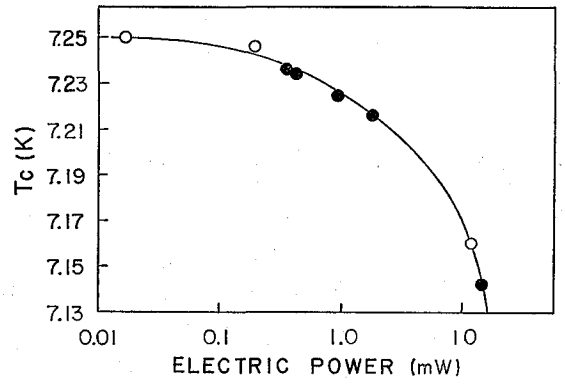

Fig. 5. T_c of lead *versus* electric power for heating.

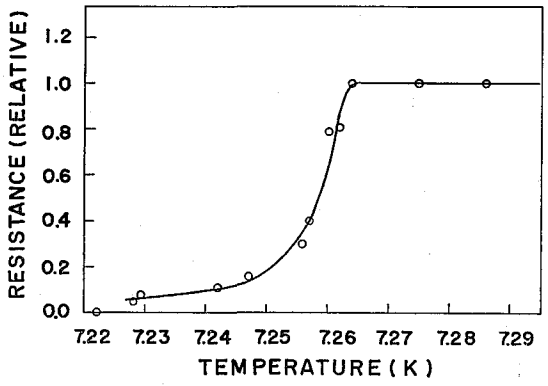

Fig. 6. Typical transition curve of lead.

relations of the observed transition temperatures of lead versus the electric power for heating are demonstrated. The typical transition curve of lead is also shown in Fig.6. From these results, T_c, of lead was determined as $7.25_7 \pm 0.01$ K, which agrees well with previous works[4~10] (See Table I).

The result with lead indicates that the present experimental procedure involving temperature control and temperature calibration is satisfactory for the measurement of the resistive transition in the temperature range of 1.7~20 K. Similar measurements were performed with technetium. Three samples were prepared; (a) by electrodeposition, (b) by electrodeposition and reduction (800°C, 1 h), and (c) by electrodeposition and reduction (1000°C, 3h). The observed transition curves

Table I. *Superconducting Transition Temperature of Lead*

Tc (K)	Method	Reference
7.22±0.03	Resistance	4
7.24	Resistance	5 (film)
7.20±0.01	Resistance	6 (wire)
7.22±0.04	Magnetic Susceptibility	7
7.175±0.005	Magnetic Susceptibility	8
7.193±0.005	Magnetic Susceptibility	9
7.155	Resistance	10
7.25_7 ±0.01	Resistance	present (film)

Table II. Superconducting Transition Temperature of Technetium

Tc (K)	Method	Reference
7.73±0.02	Magnetic Susceptibility	1
7.46±0.04	Magnetic Susceptibility	11
7.85	Magnetic Susceptibility	12
7.86	Heat Capacity	13
7.46±0.05	Resistance	present

are shown in Fig. 7. Numerical values of *Tc* are listed in Table II together with the previous results by other workers.[1,11~13]

The first sample apparently gives very low *Tc*, indicating that without the reduction procedure the formation of metallic technetium is not satisfactory. The transition curve of the second sample has a long tail in the lower temperature region. This indicates that the production of metallic technetium is not yet satisfactory for the reduction at 800°C for 1 h. The transition curve of the third sample shows that the

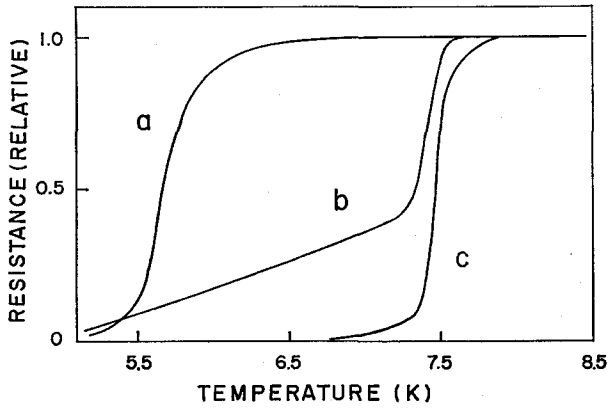

Fig. 7. Transition curves for different technetium samples prepared; a) by electrodeposition, b) by electrodeposition and reduction (800°C, 1 h), c) by electrodeposition and reduction (1000°C, 3 h).

reduction at 1000°C for 3 h is sufficient to obtain a good sample. Thus, Tc of technetium prepared by electrodeposition and reduction was determined as 7.46 ± 0.05 K. Although the present sample is prepared by the completely different method from others, our result is in line with those previously reported.

It should be noted that taking into consideration the lack of (100) peak in the X-ray differaction patern of our sample, the present sample seems to have the orientation along the c axis of the structure.

In summary, we conclude that the metallic technetium prepared by electrodeposition and reduction procedure presented here is useful for investigations of superconducting properties of the element. Studies of the magnetic properties of superconducting technetium are in progress.

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